Properties and Performance of Near UV Reflectivity Control Layers

Tom Lynch, Valerie Paradis, Mark Spak , Hoechst Celanese, Somerville, NJ 08876
and
Wayne Moreau, IBM, East Fishkill, NY 12533

ABSTRACT

Reflectivity control layers (RCL) improve linewidth control of I line resist imaging. The RCL underlayer can suppress reflective notching from underlying features and minimize the swing interference effect of varying resist thickness. A major drawback of RCL layers is the extra coat and/ or high bake step and the additional oxygen RIE step for pattern transfer unless the RCL underlayers etch faster than the resist in the gases used for substrate RIE etching. The RCL coatings are usually formulated from organic dyes dispersed in a polymeric layer at loadings of 10-50 % by weight of total solids. The polymer base is soluble in polar solvents such as cycloketones, NMP, and cyclic lactones. The polymer base is insoluble in the I line resist solvents of acetates and the like. The added dyes themselves are not necessarily insoluble in the resist casting solvent but rely on the insoluble polymer layer to inhibit dissolution. In the cast film of two component RCL underlayers, micrograms of absorbing dyes are in contact with several mls. of resist casting solvent and leaching or loss of the dyes can occur especially in sub-150 nm thick RCL underlayers. Secondly, the post-apply bake step to remove the casting solvent and temporarily seal the layer prior to resist coating adds extra cost to I line lithography resist processing.

To overcome the limitations of two component RCL formulations, we have synthesized polymeric dyes which offer no or low bake processing and have suitable I line absorbance in films less than 100 nm thick. The polymeric RCL films are synthesized from absorbing dyes which are grafted onto polymers which are insoluble in the resist casting solvents. We have utilized amine dyes which are imidized onto polymeric backbones by a one step synthesis. The peak absorbance of the grafted dye after imidization undergoes a blue shift of about 30 nm and thus appropriate H line dyes are used to achieve I line peak absorbance.

The dye is reacted directly with the polymer base at the reflux temperature of the RCL casting solvent. The kinetics of the imidization are followed by IR spectroscopy to ensure complete grafting. The synthesis affords lower costs materials and eliminates leachable dye components. By choosing a non-aromatic polymer backbone, the reactive ion etch erodability of the RCL layer is enhanced to be 1.5-2.X faster than the I line resist. The higher erodability of the RCL opens up the possibility of simultaneous reactive ion etching of the resist/RCL using halogen gases.

In practical applications, the RCL layer can reduce resist thickness/surface (swing type) interference effects to less than +/- 8 % and across the chip linewidth variations from +/- 140 nm to less than +/- 80 nm. Another useful application is the improvement of consistency of the photospeed of I line resist. The tested resist is used on top of an RCL layer to obviate the errors due to thickness interference effects. With this procedure, lot to lot consistency of +/- 1 % can be achieved. In this paper, the synthesis, properties, and performance of one component RCL layers will be discussed. The formation of a one component RCL film eliminates dye loss during baking or coating processes and allows for higher absorbance in thinner film.

1. INTRODUCTION

In the fabrication of submicron integrated circuits, the control of linewidths to smaller tolerances over topography may require auxiliary coatings or processes to minimize distortions due to interference effects and reflective notching, Figure 1. [1] The quantification of the interference effect can be measured by using the swing ratio (SR) set forth by Brunner, [2]

$$SR = 4 (R_1 R_2)^{1/2} e^{-AD}$$

where R_1 is the reflectivity of the resist/air interface and R_2 is the reflectivity of the resist/substrate interface, A is the resist absorbance and D is the resist thickness, Figure 2. Various methods to reduce the swing ratio interference effects are shown in Figure 3, include dyed resist [3] to enhance (A), topcoat reflectivity control layer [1] to reduce R_1, and various thick or thin bottom reflectivity control layers(RCL) to eliminate R_2. To reduce reflective notching, dyed resist and bottom RCL are used. [4]

The bottom RCL layers can effectively reduce both interference and reflective notching without the image distortion of dyed resists and also enhance depth of focus about 15 %.[5]The formulation of bottom RCL comprise organic dyes[6] dispersed in polymers which are insoluble in the usual resist casting solvents of esters such as 2-methoxypropyl acetate(PMA) or ethyl lactate. In two component RCL, the polymer base acts as a barrier to solvent extraction of the added I line dye. The added dyes and polymer bases should be thermally stable to withstand bake processes.The effective absorbance of two component RCL relies upon high loading > 20 % by weight of solids and sufficient film thickness > 100 nm to retain an effective processing layer. Associated with these formulations are potential dye agglomeration and self-limiting absorbance[7], dye precipitation[8], and dye susceptibility to resist solvent extraction or loss by sublimation, Figure 4.[6] In addition, the use of films > 150 nm in thickness increases the biases of reactive ion etch (RIE) transfer especially if the RCL etches at the same rate as the overlying aromatic novolak resists.

To overcome the limitations of two component RCL, we have investigated the synthesis and direct formulation of one component RCL for I line application or other exposure wavelenghts (deep UV or G line). The one component approach is to bond a suitable chromophore to a polymer resistant to resist solvents. The polymer itself is aliphatic in nature to enhance the possibility of direct RIE etch transfer in the gases used for substrate RIE .

The design consideration of the one component RCL set targets of :
a. No / or Low bake process.
b. RIE etch rate > 1.5 X of Novolak.
c. Resistant to casting solvent/ alkaline developer.
d. Absorbance > 10/um (processable < 100 nm thickness).
e. Edge Bead Removable in cycloketones,NMP or lactones.
f. Highly uniform cast films (< +/- 10A).
g. Low Cost and shelf life > 1 yr at 20C.

2.EXPERIMENTAL-

The synthesis of the one component RCL involves the reaction of a primary amine dye with an anhydride group to form an imide,
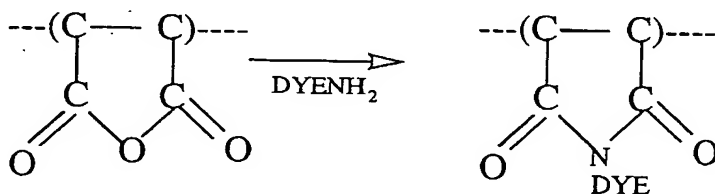
The synthesis is performed as a one pot reaction in a suitable solvent such as cyclohexanone. Over a period of several hours at constant reflux temperature, the reaction proceeds to completion.The solution after filtration and dilution is used directly as an RCL.

The kinetics of conversion were performed by IR spectroscopy, Figure 5, to follow the imidization in the 1600-1700 cm^{-1} carbonyl region. Fragmentation mass spectroscopy was used to confirm the dye attachment to the polymer backbone.Thermal analysis of dye bonded films was performed by UV, IR, and TGA analysis and indicate stability to 300 C. Extraction of dye components were tested by soaking films in resist casting solvents and examining dye retention by UV absorbance and film thickness. No loss of dye in PMA resist solvent is noted after completion of reaction, Figure 6. The cast film is soluble in cycloketones,lactones, or NMP for simultaneous edge bead removal of I Line resist/RCL. The spin coating standard deviation for a 100 nm film thickness is <+/- 5A.

The shelf life of the bonded dye was tested by accelerated aging at 55C for absorbance loss and after refrigeration test for precipitation. The projected shelf life of RCL-365 is at least one year at 20C. The spectral reflectance of RCL films on substrates were examined by a Hewlett Packard UV reflectometer. The refractive index of RCL-365 was determined to be 1.902 at 365 nm using a RUDOLPH ellipsometer in conjunction with a NANOSPEC film thickness instrument. The resist applications of RCL involving RIE were performed on AME RIE system. In conjunction with a I line Novolak based resists , studies of swing reduction, step interference reduction and reflective notching were performed.

3.RESULTS and DISCUSSION-

The formulation of RCL coatings usually involves mixing of a absorbing dye with a polymer that is resistant to resist solvents such as PMA and ethyl lactate and alkaline developers (for RIE developable systems). The dyes themselves are not necessarily insoluble in the ester solvents but soluble in more polar RCL solvents such as cycloketones or lactones. The solvent resistance of the cast RCL films relies primarily on the excess polymer encapsulating the added dye. Spin coating of thin films especially < 100 nm thick can result in an inhomogeneous distribution of dyes in the polymer in the RCL film.[9]

Formulations which load polymers with dyes depends on the polymer acting both as a solvent and an impermeable barrier to casting solvent penetration and leaching. Secondly, in order to obtain sufficient absorbance (B > 10/um) in films of the order of 100 -200 nm thick, dye loadings can lead to dye aggregation and phase separation during spin coating [7] and further susceptibility to solvent attack. Although the dye may exhibit low solubility < 1 % by wt in the resist casting solvent, the leachability of the dye is evident in film thickness dependency of PMA extraction. In this case, Figure 7, a PMA insoluble dye is loaded to 20 % by weight in polymethyl methacrylate. The films are baked at 150 C for 2 minutes and tested for dye leaching by UV absorbance before and after coating with the resist casting solvent of PMA. The loss of dye increases with decreasing film thickness. A possible explanation for the loss of dye in ultrathin RCL films is the preferential alignment of the polymer chains in thin films which allows them to extend out and hydrogen bond to more solvent than a corresponding thicker films.[10] Preferential bonding to the dye is reduced and the micrograms of dye in contact with grams of casting solvent diffuse into the liquid phase. The one component dye bonded RCL-365 shows no sign of dye loss at any thickness in the 20-200 nm range. In addition, the RCL-365 is thermally stable to 275 C for such applications as a thick underlayer for bilayer or as a polymer release layer for stripping ion implanted resists.

The bonding of the dye involves the imidization insertion reaction. The choice of bonding dye for RCL I line or G line absorbance depends on the chromophore and the conjugation responsible for example for 365 nm absorbance. Various amino dyes conjugated to anthraquinone, azo, and ketones were examined as suitable absorbers. If the amine group was attached to a chromophore such as in an azo dye,

$$H_2NRN=NR$$

spectral shifts were noted, Figure 8, after imidization. In this case a blue shift from an initial H line (405 nm) absorbance to I line (365 nm) was noted. In order to achieve very high absorbances > 20/ um at 365 nm or 30/um at 248 nm, blended dyes with high extinction coefficient (100,000 l/mole cm) are required in a two component RCL or in the case of a polymeric RCL the complete imidization of a polyanhydride polymer is required. However, incorporation of large amounts (> 50 mole %) of aromatic type dyes decreases the reactive ion etch rate of the RCL. One of the desired features of a RCL is the ability to reactive ion etch through the 75-150 nm layer directly using Al and Si halogen RIE gases or with minimum biases with O_2 RIE.

It has been established that aliphatic type polymers such as PMMA etch 1.5-3X faster than novolak resins. [11] Thus, ideally an all aliphatic RCL without any aryl groups would etch faster than novolak resins. However, to satisfy the absorbance requirements, aromatic chromophores are generally required. The net results of the RCL-365 composition was an polymer with RIE characteristics of 1.7 X faster etch rates than novolak resists, Table 1.

Table 1- RIE Etch Rates in AME Reactors Relative to NOVOLAK, PMMA, and Phenyl Methacrylate (PhPMMA)

Film	Al Cl Etch	Si CF$_4$ etch	O$_2$ etch
NOVOLAK	1.0	1.0	1.0
RCL-365	1.7	1.6	1.7
PMMA	2.2	1.9	1.9
PhPMMA	1.7 +/-0.1	1.6+/-0.1	1.5 +/-0.1

As device dimensions continue to shrink to 500 nm, the patterning of lines over substrates of variable reflectivty suffers from reflective notching and more CD variations. The major benefit of the use of

a RCL layer is the significant reduction in reflectivity to less than 10 % on most of the semiconductor surfaces. The reduction, for example, of the reflectivity at 365 nm, Figure 9, as measured by a scanning reflectance is below 4 % at 365 nm with a B/um of 14 for the bleached I Line resist/RCL(P/R) RCL-365 layer. The RCL-365 reduces the linewidth variation, Table 2, to less than +/- 2 %.

Table 2- Comparison of Images With and Without RCL-365

Resist Thickness	Resist only Linewidth	Resist/RCL Linewidth
1.125 um	0.72 um	0.73 um
1.150 um	0.79 um	0.73 um
1.168 um	0.87 um	0.76 um
1.178 um	0.97 um	0.77 um
1.201 um	0.94 um	0.76 um
1.224 um	0.86 um	0.75 um
1.254 um	0.79 um	0.74 um
Std Dev.	+/- 0.089 um	+/- 0.013 um

Images over steps suffer from variable resist thickness and distortion,Figure 1. An example of elimination of step interference of 550 and 650 nm lines with RCL underlayer can be seen in Figure 10. The reflective notching of lines over polysilicon surfaces, Figure 11, is corrected with an RCL underlayer. For actual device application, the control of linewidths across the chip itself is subject to distortions due to substrate reflectivity, lens distortions resist thickness variations, developer action, and RIE inhomogeneity which all contribute to excess across chip linewidth variation (ACLV).[12] The use of a RCL layer, Figure 12, reduces the totals ACLV by a factor of 2 from +/- 140 nm to +/- 70 nm.

To simulate the reflectivity reduction, modeling of stacks of I line resist/ RCL reveals, Figure 13, different optimum thicknesses for substrates of Al, silicon, and polysilicon. Since Al films have significantly lower refractive index and higher reflectivity, a RCL of 150 nm thickness will provide the lowest reflectivty. Thinner films of 80-90 nm can be used on silicon type surfaces.

Lastly, another practical application of the use of a RCL layer is in the quality control of production of photoresist and as an exposure monitor for exposure tool or litho process setup. The use of an RCL makes the photolith process practically independent of the substrate type or thickness of the photoresist. Based on this insensitivity, a simple exposure monitor of resist/ RCL can be used for setup or monitoring.In the production of lots of photoresists, the measurement of the lot to lot photospeed is subject to the precise control of the resist thickness to less than +/- 2.5 nm. On bare silicon monitor wafers it is difficult to achieve better than +/- 3 % in determining and qualifying the photospeed (dose to clear, E_0) of a resist.[13] The use of a RCL-365 layer significantly reduces the thickness errors, Figure 14, to achieve +/- 1 % E_0 lot to lot photospeed.

4.SUMMARY-

Reflectivity control layers (RCL) improve linewidth control of I line resist imaging. The RCL underlayer can suppress reflective notching from underlying features and minimize the swing interference effect of varying resist thickness. A major drawback of some RCL layers is the extra coat and/ or high bake step and the additional oxygen RIE step for pattern transfer unless the RCL underlayers etch faster than the resist in the gases used for substrate RIE etching. To overcome the limitations of two component RCL formulations, we have synthesized polymeric dyes which offer no or low bake processing and have suitable I line absorbance in films less than 100 nm thick.

The polymeric RCL films are synthesized from absorbing dyes which are grafted onto polymers which are insoluble in the resist casting solvents. We have utilized amine dyes which are imidized onto polymeric backbones by a one step synthesis. The dye is reacted directly with the polymer base at the reflux temperature of the RCL casting solvent. The kinetics of the imidization are followed by IR spectroscopy to ensure complete grafting. The synthesis affords lower costs materials and eliminates leachable dye components. By choosing a non-aromatic polymer backbone, the reactive ion etch erodability of the RCL layer is enhanced to be 1.5-2.X faster than the I line resist. The higher erodability of the RCL opens up the possibility of simultaneous reactive ion etching of the resist/RCL using halogen gases.

In practical applications, the RCL layer can reduce resist thickness/surface (swing type) interference effects to less than +/- 8 % and across the chip linewidth variations from +/- 140 nm to less

than +/- 70 nm. Another useful application is the improvement of consistency of the photospeed of I line resist. The tested resist is used on top of an RCL layer to obviate the errors due to thickness interference effects.

5. ACKNOWLEDGEMENTS-

6. REFERENCES-

1. S.Miura, C. Lyons, and T. Brunner, SPIE Proc., 1764, 147(1992).
2. T.Brunner, SPIE Proc., 1466, 297 (1991).
3. B. Daniels, and P. Trefonis, J. Elec.Soc. 135, 2319(1988).
4. M. Horn, Solid State Technology, Nov., 1991, p. 57.
5. Y.Mimura and S. Aoyama, Microelectronic Eng., 21, 47(19 93)..
6. US patents, 4,668,606(1987) and 5,126,289(1992).
7. K. Law, Polymer, 23, 1627(1982).
8. P. Paniez and G. Amblard, Microelectronic Eng., 5, 32(1986).
9. D.Funhoff, H. Binder, and R, Schwalm, SPIE Proc., 1672, 49(1992).
10. V. Rao, W. Hinsberg, W. Franck, R. Pease, SPIE Proc., 1925 538(1993).
11. W. Moreau, SEMICONDUCTOR LITHOGRAPHY, Plenum Press, 1989, p.730.
12. N.Samarakone, etal., SPIE Proc., 1463, 16(1991).
13. W.Conley, N.Eib, M.Plat, and R. Smith, OCG INTERFACE 93 Proc., p.29.